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Possible techniques for the detritiation of first wall materials from fusion machines

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Abstract

Tritium in first wall materials of fusion machines is a matter of concern not only for inventory purposes but also for safety reasons. In the first wall carbon tiles, tritium is found predominantly in a very thin codeposited layer and/or implanted in the surface layers. Since the tiles must eventually be disposed off in a repository it is desirable to reduce the total tritium inventory in the tiles down to the corresponding low level waste category. In this context, the development of detritiation techniques for graphite and CFC tiles removed from the first wall of fusion machines is of paramount importance. However, the experimental techniques investigated until now are limited by the conditions and techniques permissible inside the torus. Nevertheless, for tiles removed from the reactor more severe treatment techniques are acceptable. Working in that direction, numerous screening tests have been carried out at the Tritium Laboratory in Karlsruhe (TLK).

1. Introduction

In graphite tiles of the first wall of D-D and D-T operated fusion machines tritium is found predominantly in a very thin co-deposited layer and/or as an implanted layer with a thickness of few tens of micrometers. Smaller tritium concentrations are retained into the bulk of the tiles after diffusion via the surface connected porosity and by transgranular diffusion. After a shut-down of a fusion machine it will be necessary to reduce the tritium concentration in the tiles to very low levels either to allow their reuse or to condition them for final disposal. In the latter case it is important to reduce the total tritium concentration in the tiles down to levels corresponding to those of the category ‘low level waste’ (LLW) (12 MBq/kg in UK). To accomplish this it is necessary to develop simple, reliable, and effective detritiation technologies allowing the conditioning of a large number of graphite and CFC tiles.

Most activities to date in the field of graphite tile detritiation have concentrated on in situ methods, i.e. those performed inside the reactor, having the main objective of reducing the total in-vessel tritium inventory. Correspondingly, the work has been limited to gas-solid treatments under conditions restricted by the parameters permissible inside of the reactor and by the current safety requirements. Deuterium or oxygen–helium glow discharge cleaning at moderate temperatures, disruption discharge cleaning, as well as air purges at moderate temperatures have been employed [1,2]. Another recently proposed approach is the treatment of the tile surface with an impinging laser beam under an inert gas atmosphere [3,4]. When dealing with the tiles outside of the reactor more severe treatment techniques

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are acceptable, not only because single tiles or packages can be treated, but also because no precautions concerning the structural parts of the machine need to be taken.

In this work the main effort has been directed towards a tile treatment ex situ with a view to final disposal. For that reason not only gas/solid techniques have been examined, but also methods involving liquid phase treatment of the tiles.

2. Experimental techniques

The experimental techniques employed to investigate graphite detritiation are described briefly below.

2.1. The preparation of samples

To determine the actual concentration of tritium in the bulk of a tile the face opposite to the one exposed to the plasma was first cleaned with alcohol to remove all surface particles possibly contaminated with tritium. Next, a 7.6 mm cylinder was cut starting from this face of the tile using a fresh core drill. The cylinder produced was then retrieved and twelve nearly equal sized 1 mm thick disks were cut from this cylinder. Each disk was submitted to a detritiation technique among those mentioned below and then fully oxidised with moist synthetic air at 850 °C employing a technique described in detail in Ref. [5] in order to account for its total tritium content. To completely exclude cross contamination from previous tritium analyses the glass/quartz apparatus was thoroughly cleaned after each measurement and a full background determination was performed to confirm it as tritium-free. The tritium released by slow and complete combustion was collected in a water bubbler and analysed by liquid scintillation counting.

2.2. Ultrasonic bath treatment

The graphite or CFC disks were introduced into a 250 ml Erlenmeyer flask provided with a cap and containing either water or hydrogen peroxide and then placed into the water of an ultrasonic bath (Super Sonorex RK103H). The disks were treated at temperatures in the range 50–70 °C for a period up to 1 h.

2.3. Detritiation with moist air or nitrogen

To investigate the detritiation of graphite tiles with moist air or nitrogen A1 disks (the first millimetre from the surface from the plasma-exposed side of a graphite tile) were introduced into a quartz tube inside an oven as described in Ref. [5]. Temperatures were measured using a thermocouple placed on top of the graphite specimen. Synthetic air from a pressurised cylinder was first passed through a water bubbler and then over the sample.

The sample was placed in the Vance apparatus [6] at ambient temperature above the oven zone and moist air was passed over it (10 cm^3/min) for a specified period. At the same time the oven was kept at 850 °C to assure complete combustion of all the released hydrocarbons. After a specified period the same graphite disk was then introduced into the heated zone of the oven while the temperature was increased in steps up to 400 °C.

The tritium released was measured using two consecutive bubblers, each containing 50 ml of water, placed downstream of the reactor. The tritium remaining in the disk after the exposure to moist air to temperatures up to 400 °C was measured by full combustion of the disk.

2.4. Detritiation with moist ozone

To determine the tritium release achievable by treatment with ozone, a disk from the plasma-exposed side of a graphite tile from JET was subjected to an oxygen stream containing ozone using an experimental apparatus shown schematically in Fig. 3 of Ref. [5]. Ozone was generated with a Fisher ozone generator yielding ≈ 1 g O_3/h at an oxygen flow rate of 30 l/h ($\approx 1.6\%$ O_3 in O_2). The oxygen/ozone stream was humidified by passing the gaseous mixture through a bubbler containing water. Downstream of the oven the exhaust gas was passed through two consecutive bubblers, a first one containing 50 ml water and a second one containing 20 g/l potassium iodide dissolved in water (pH = 7).

2.5. Detritiation with moist noble gases employing radio frequency heating

A metal reactor with a feed through for a water-cooled radio frequency (RF) coil was used for these experiments. A schematic drawing of the equipment is shown in Fig. 1. Graphite samples were placed in a quartz tube placed axially inside of the copper RF coil. A quartz wool filter maintained the graphite specimen at the desired position. The quartz tube was joined to the inlet stainless steel tube via a metal/glass/quartz transition joint. The graphite itself was the susceptor for the RF heating power. By this procedure the graphite disks could be heated very rapidly to high temperatures measured with a pyrometer. The thermally released tritium is purged by humidified argon (99.999% purity in entrance) used as carrier and passes sequentially through a heated quartz tube containing a BASF R3-11 catalyst bed (Cu_2O/CuO) where it is oxidised to water and collected downstream in 2 bubblers filled with 50 ml water.

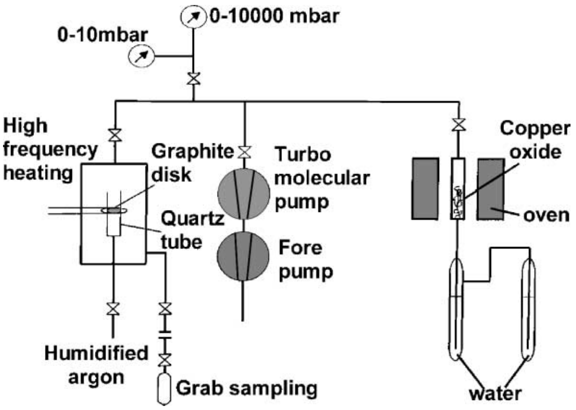

Fig. 1. Schematic set-up of the apparatus used to heat graphite samples by RF heating.

2.6. Detritiation with an open flame

Another technique tested consisted of exposing the surface of the plasma-exposed side of a TFTR tile to the open premixed flame of a burner supplied with acetylene and nitrous oxide. To this effect the surface of the disk was treated for a few seconds with the hottest zone of the flame. The weight of the disk was determined before and after the treatment. The effectiveness of the treatment was derived from a comparison between the known mean tritium concentration of TFTR disks as determined previously [5] and the tritium concentration found by full combustion after brief exposure to the flame.

3. Results and discussion

3.1. Ultrasonic bath treatment

After the ultrasonic treatment the liquid was filtered out and analysed for tritium and the filter paper was analysed by full combustion. The tritium remaining in the disk was also determined by the same procedure, i.e. full combustion combined with liquid scintillation counting. The weight of the disk was determined before and after the ultrasonic bath treatment.

The results obtained from the ultrasonic bath treatment are described in Table 1. As is apparent, this treatment does not appear to be very promising. Even in a highly reactive medium like hydrogen peroxide (30%) only a relatively minor fraction (≃11%) of the tritium is liberated into the liquid.

Table 1
Detritiation of disks from TFTR tile using an ultrasonic bath

Conditions of the ultrasonic treatment	Activity in water (%)	Activity in filter (%)	Remaining activity (%)
50 °C/15 min in H_2O	1	7	92
70 °C/1 h in H_2O	1	16	83
50 °C/15 min in H_2O_2	5	6	89

3.2. Detritiation with moist air or nitrogen

Prior to the detritiation runs a graphite disk from the plasma-exposed side of tile 004/2-20 was placed in the Vance apparatus and treated as described above (Section 2.3). The amount of tritium released under the first step was very small, i.e. 0.3%, indicating that at room temperature the tritium remains trapped. There is no weight lost during this step. After exposure to increasing temperatures, the tritium release increases according to the temperature but independently of time. The largest fraction of tritium was obtained at 400 °C. The comparatively large loss of weight observed during that step strongly suggests that under these conditions the disk begins to combust. In a final run carried out at 850 °C, the sample was completely combusted and the remaining fraction of tritium collected in the bubblers. Fig. 2 illustrates the whole experiment.

Another sample was thermally treated in a thermobalance (Netzsch). The specimen was first heated under a humidified nitrogen stream at 350 °C for a total of five hours and then replaced by moist air keeping the other parameters constant. Under these conditions, 59% of the trapped tritium was released in the first step and only an additional 3% after the gas exchange, thus illustrating the importance of water regardless of the carrier gas.

Similar observations have been reported by Causey et al. [7,8] in their studies with co-deposited and implanted material. Their tritium release results have

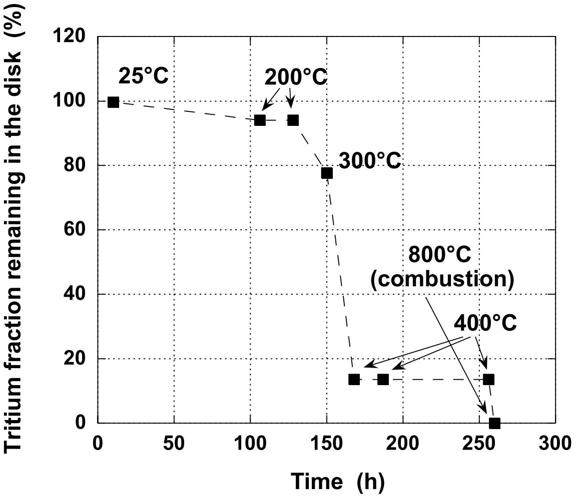

Fig. 2. Tritium release by sweeping the surface of a plasma-exposed graphite disk to moist air.

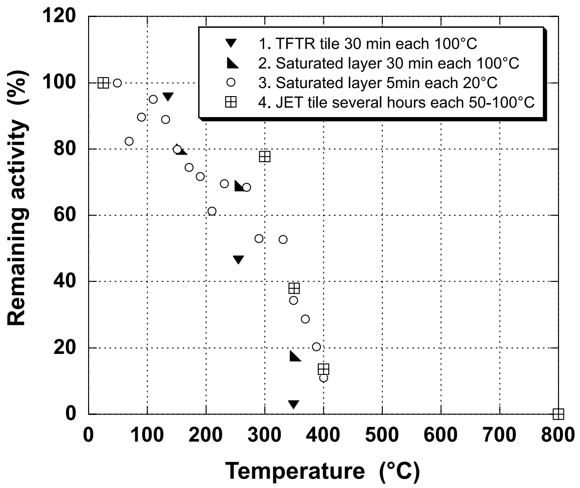

Fig. 3. Tritium release from saturated layers and co-deposited films from JET and TFTR. 1–3 (7, 8) 4 this work.

been plotted together with those obtained in this work in Fig. 3.

Replacement of air by nitrogen does not appear to have a significant effect on the fraction of released tritium. According to Ref. [7] and depending upon the experimental arrangement a complete fractional release of tritium can be achieved after only 5 min. Thus for a rapid and quantitative liberation of the tritium co-deposited on a tile a short exposure to moist air at a temperature of the order of 400 °C will have to be contemplated.

3.3. Detritiation with moist ozone

Passing ozone over a carbon disc has produced only minor releases of tritium (max. 6%). This can be attributed to two facts, firstly the presence of water hinders the ozone reaction with the sample; ozone reacts preferentially with water rather than the sample. Secondly, passing ozone through a heated quartz tube decomposes it thermally according to the following reaction mechanism: $2O_3 \rightarrow 3O_2$.

Clearly, as the temperature is raised, the fraction of ozone available for reaction with the co-deposited layer becomes smaller. Theoretical calculations for our quartz tube configuration indicated that above 250 °C all the ozone is converted to oxygen. The small release of tritium observed could be caused by ozone, exchange with moisture or some other oxidation mechanism. More work is needed to clarify this issue.

3.4. Detritiation with moist noble gases under RF heating

Under the assumption that the type of carrier gas for the moisture is of minor importance (see Section 3.2) some tests were carried out using argon as carrier gas. The prospect of avoiding oxygen has the potential advantage of a tritium release without graphite combustion and therefore without damaging the tile. In addition, the need to deal with tritium contaminated carbon oxides in the exhaust stream is avoided.

The specimens were heated in these experiments by RF heating in a stainless steel apparatus (Fig. 1). In the first run, an A1 disk (59.50 mg) obtained from the plasma exposed side of cylinder no. 35 drilled from tile 004/2-20 was introduced into the axial quartz tube inside the apparatus. The whole reactor was then evacuated to remove oxygen. Then argon saturated with moisture was introduced into the reactor and the gas flowed through at a rate of 15 cm^3/min over a period of 65 h. Only 0.3% of the tritium was released under these conditions. The disk was then heated very rapidly by RF heating up to 850 °C. The fraction of released tritium with time was determined by periodically changing the bubblers, initially after 30 min and then after more prolonged periods of time (see Table 2). Of the total activity in the disk

Table 2
Tritium release from a plasma-exposed disk obtained from cylinder 35 of JET tile 004/2-20 employing RF heating and a moist Argon sweep stream

Bubbler	Temperature (°C)	Accumulated heating period (h)	Fraction of released activity (%)	Fraction of activity remaining in disk (%)
1	23	65.0	0.3	99.7
2	850	0.5	49.3	50.7
3	850	1.0	80.7	19.3
4	850	1.5	89.4	10.6
5	850	2.0	92.6	7.4
6	850	2.5	94.1	5.9
7	850	3.5	95.1	4.9
8	850	4.5	95.5	4.5
9	850	6.0	95.9	4.1
10	850	24.0	96.3	3.7[a]

[a] Fraction remaining in the thin disc.

Table 3
Tritium activity in the thick and the thin disk produced after RF treatment

Disk mass (mg)	Released activity (Bq)	Mass specific activity (Bq/g)
52.55	0	0
0.25	123	4.9×10^5

not more than 96.3% is liberated even after 24 h at 850 °C when moist argon is used as carrier gas.

When the reactor was opened it was observed that a very thin disk (weight 0.25 mg) had spalled off from the main disk. The registered weight loss of the thick disk was determined to be 6.7 mg indicating that a portion of the thin disk had been consumed. To determine the tritium content, both disks were combusted separately. The measured tritium concentrations in the two disks have been tabulated in Table 3. It is seen that all of the remaining activity is concentrated in the thin disk. From this observation could be concluded that the spalled-off disk actually consists of the co-deposited layer. It appears that under the prevailing conditions 850 °C is sufficient to remove all the bulk tritium but not all of the tritium in the co-deposited layer. This supports previous suggestions that hydrogen in the co-deposited layer is strongly bound in the form of covalent chemical bonds [9].

3.5. Detritiation with a flame

Disks obtained from the plasma-exposed side of a TFTR tile were treated in a few runs with an open flame for a few seconds and the remaining tritium was measured by the full combustion technique. It was observed that more than 98% of the tritium can be liberated by this hard but short treatment within a very short time. Thus, this treatment can be considered as highly promising for the detritiation of tiles before final disposal.

Conceivably, the tiles could be passed under a flame crown or exposed to a rectangular burner in an appropriate closed oven while continuously sweeping with an appropriate moist gas (or gas mixture) stream. A heated copper oxide bed downstream could ensure that all tritiated species and carbon monoxide are quantitatively oxidised to water and carbon dioxide. Water could be trapped, very efficiently in a type 3A zeolite molecular sieve bed, this type is proposed because it will essentially not retain carbon dioxide.

4. Evaluaxtion of the investigated detritiation techniques

The ultimate goal of this waste conditioning investigation is an assessment of the effort needed to achieve the 'solid low level radioactive waste category' for the graphite tiles of JET. In the UK solid waste having a specific activity higher than 0.4 Bq/g and below 12 MBq/kg of non-alpha emitting radionuclides falls under this category [10].

The most promising techniques appear to be:

- Abrasive removal of the co-deposited layer from a tile with a metal brush or an abrasive paper.
- Treatment of a whole tile with humidified air at temperatures of 500 °C or above.
- Short treatment of the plasma-exposed side of a tile with an open flame or alternative flash heating procedures.

In addition, the exposure of an RF heated tile to a humidified noble gas has also yielded encouraging results. These and other techniques, such as the use of an argon torch [11], will now be tested in the near future on whole tiles or large fragments of them.

5. Conclusions

Graphite tiles used in fusion devices such as JET operated with a D-D or a D-T plasma contain tritium. In graphite tiles most of the tritium (about 99%) is found in a thin layer of less than 50 μm on the plasma-exposed side of the tile. The rest of the tritium (about 1%) is evenly distributed within the bulk of the tile. For CFC tiles a large fraction of the tritium is trapped in the bulk. The detritiation techniques described in the paper (except full combustion) are almost exclusively dedicated to the detritiation of the surface co-deposited layer.

Treatment of plasma-exposed graphite in an ultrasonic bath containing water or hydrogen peroxide proved to be a rather ineffective detritiation method.

A humidified ozone/oxygen stream causes only minor liberation of tritium co-deposited with carbon at temperatures in the range 25–200 °C. Increasing ozone decomposition rates with increasing temperatures (nearly complete at temperatures of about 200 °C) constitute the limiting factor for this technique.

In laboratory experiments, a sizeable fraction of the tritium in the co-deposited layer of tile sample is released by heating up to about 400 °C under a stream of moist synthetic air or nitrogen. The release of tritium is predominantly determined by the temperature and to a lesser extent by the duration of the heating. With RF heating at 850 °C under a humidified noble gas stream it is possible to achieve high tritium decontamination factors. Further research shall uncover the full potential of the technique. The quick treatment of the plasma-exposed side of a graphite specimen with an open acetylene flame proved to be very successful.

Alternative flush heating procedures should also be explored, which may have reduced hazards associated with them.

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